PHYSICAL CHEMISTRY

A. V. KISELEV and D. P. POSHKUS

1958

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

A. V. KISELEV and D. P. POSHKUS

THE ENERGY OF THE COULOMB INTERACTION OF A HYDROXYL GROUP OF SILICA GEL WITH A BENZENE MOLECULE

(Presented by Academician A. N. Frumkin, 18 I 1958)

As has been established in a number of works from our laboratory, the adsorption of benzene vapor on silica gel whose surface is almost completely covered with hydroxyl groups is considerably higher than the adsorption on silica gel from whose surface the hydroxyl groups have been partially removed by calcination ($^{1-3}$). The heat of adsorption of benzene vapor on a hydrated silica-gel sample at a surface coverage $\theta = 0.2$ is higher than on a strongly dehydrated one by approximately 2-3 kcal/mole (^{2,4}). The increase in adsorption and in the heat of adsorption of benzene vapor on hydrated silica gel, as compared with the adsorption and heat of adsorption on dehydrated silica gel, is explained by the formation of a hydrogen bond between the surface hydroxyl groups of silica gel and the π-electrons of the adsorbed benzene molecules (^{5}). Spectroscopic data also indicate the ability of the benzene molecule and of other aromatic compounds to form a hydrogen bond with an acidic hydroxyl group ($^{6-10}$). According to the electrostatic theory of the hydrogen bond, its energy is due mainly to the electrostatic attraction of the dipoles or residual charges of the interacting groups. In the present work an attempt has been made to estimate the energy of the Coulomb interaction of a hydroxyl group of silica gel with an adsorbed benzene molecule, in order to elucidate the role of this interaction in the formation of a hydrogen bond between the hydroxyl group and the benzene molecule*.

The energy of the Coulomb interaction of two molecules has been calculated by a number of authors ($^{11-16}$). An exact calculation of the energy of electrostatic interaction of two molecules must take into account the electrostatic interaction of their nuclei and of the electron clouds of all orbitals of both molecules (^{16}). However, such a calculation is very complicated, and in calculations of this interaction various models are usually used which approximately reflect the charge distribution in the interacting molecules.

The energy of the Coulomb interaction of the hydroxyl group with the σ-electrons and with the positive residual nuclear charges of the carbon and hydrogen atoms associated with them in the adsorbed benzene molecule is small and, to a first approximation, may be neglected, since the electron density of the σ-electrons is concentrated in the plane of the nuclei of the carbon and hydrogen atoms of the benzene molecule, while the hydroxyl group of silica gel (the dipole) is located beneath this plane.

According to the concepts of quantum chemistry, the π-electron clouds in the benzene molecule extend along the entire perimeter of the benzene ring above and below it, and the distribution of the electric charge of the π-electrons and of the residual positive charge of the carbon nuclei in the benzene molecule can be roughly represented by means of the model shown in Fig. 1a. In this model, the regular hexagon of the arrangement of the carbon atoms in benzene is, for simplicity, replaced by a circle of radius $R = 1.4$ Å, approximately equal to the length of the C—C bond in benzene. The distance of the circles representing the π-electron clouds from the plane of the benzene ring is taken equal to the mean distance of one half of the p-electron cloud of an isolated carbon atom from the nucleus $\bar{r} = 0.81$ Å, estimated with the aid of the one-electron atomic function for the $2p_z$-electron

$$\psi_{2p_z} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{5/2} r e^{-\frac{Zr}{2a_0}} \cos\theta$$

from the relation:

$$\bar{r} = \int \psi_{2p_z}^2 r^3 \sin\theta \, dr \, d\theta \, d\varphi,$$

where a_0 is the radius of the Bohr orbit, equal to 0.529 Å, and $Z = 3.25$ is the effective nuclear charge estimated by Slater' s method [17]. It is assumed that the charge of the π-electrons, $6e$, where e is the electron charge, is distributed uniformly over the circles, so that its density is

$$\sigma = \frac{3e}{2\pi R}.$$

The residual positive charges of the carbon nuclei associated with the π-electrons are equal in absolute magnitude to the electronic charge e and are indicated in the figure by black dots.

Fig. 1. Model of the distribution of electric charge in the benzene molecule (a) and in the hydroxyl group (b), and the dependence of the Coulomb interaction energy of the benzene molecule with the hydroxyl group Φ_C on their relative position (c): circles for $z_{\mathrm{H\ldots C}} = 2.15$ Å, triangles for $z_{\mathrm{H\ldots C}} = 3.05$ Å.

---

* A report on this work was made by D. P. Poshkus at the Conference on Sorbents in Leningrad on December 6, 1957.

Fig. 1. Model of the distribution of electric charge in the benzene molecule (a) and in the hydroxyl group (b), and the dependence of the Coulomb interaction energy of the benzene molecule with the hydroxyl group Φ_C on their relative position (c): circles for $z_{\mathrm{H}\dots\mathrm{C}} = 2.15$ Å, triangles for $z_{\mathrm{H}\dots\mathrm{C}} = 3.05$ Å

Figure 1: Fig. 1. Model of the distribution of electric charge in the benzene molecule (a) and in the hydroxyl group (b), and the dependence of the Coulomb interaction energy of the benzene molecule with the hydroxyl group Φ_C on their relative position (c): circles for $z_{\mathrm{H}\dots\mathrm{C}} = 2.15$ Å, triangles for $z_{\mathrm{H}\dots\mathrm{C}} = 3.05$ Å

The hydroxyl group in our calculations was considered as a system of two point charges whose positions approximately coincide with the positions of the nuclei of the oxygen and hydrogen atoms (Fig. 1b), with the effective charges of the hydrogen atom q_H and oxygen atom q_O determined from the relation $\mu = ql$, where μ is the dipole moment of the hydroxyl group and l is the internuclear distance. For the hydroxyl group on the surface of silica gel the value $\mu = 1.6D$ was adopted, approximately equal to the dipole moment of the hydroxyl group in the water molecule [18], since the electronegativities of the hydrogen and silicon atoms are close (respectively 2.1 and 1.8 [19]) and $l = 0.97$ Å. Hence $q_H \approx q_O = 1.6 \cdot 10^{-10}$ e.s.u.

The energy of Coulomb interaction of the hydroxyl group with the benzene molecule Φ_C, upon replacing the actual distribution of electric charge in them by the models adopted above, is given by the following expression:

$$-\Phi_C = \sum_{i=\mathrm{H};\mathrm{O}} \sum_{j=\mathrm{I};\mathrm{II}} \sigma q_i \int \frac{ds}{r_{i-j}} + \sum_{i=\mathrm{H};\mathrm{O}} \sum_{k=1}^{k=6} e q_i \frac{1}{r_{i-k}},$$

where the first term on the right-hand side expresses the energy of the Coulomb interaction of the effective point charges of the hydroxyl group, q_{H} (the positive effective charge of the hydrogen atom) and q_{O} (the negative effective charge of the oxygen atom), with the charge of the π-electrons of the benzene molecule, distributed uniformly over the lower (I) and upper (II) circumferences; and the second term is the energy of the Coulomb interaction of the same effective point charges of the hydroxyl group with the residual positive charges of the carbon nuclei ($k = 1, \dots, 6$); ds is the differential of the arc of the circumference, r_{i-j} and r_{i-k} are the distances between the effective point charge of the hydroxyl group i ($i = \mathrm{H};\ \mathrm{O}$) and, respectively, any point on circumference j ($j = \mathrm{I};\ \mathrm{II}$) or the positive effective charge of the nucleus of a carbon atom C. The first term is readily reduced to an elliptic integral, while the second was calculated by numerical summation.

The energy of the Coulomb interaction was calculated for the perpendicular orientation of the hydroxyl group to the plane of the benzene ring (the energetically most favorable orientation) for the following positions along the radius ρ

passing through the nucleus of a carbon atom: under the center of the benzene ring, $\rho = 0$; under the center of a carbon atom, $\rho = R$; under points located outside the benzene ring at distances $\rho = 1.5R$ and $\rho = 2R$ from its center. The equilibrium distance $z_{\mathrm{H\ldots C}}$ from the nucleus of the hydrogen atom of the hydroxyl group to the plane of the ring of carbon atoms of the benzene molecule is unknown. Therefore the calculation of Φ_{C} was carried out for two possible limiting values of $z_{\mathrm{H\ldots C}}$: 2.15 Å and 3.05 Å, equal to the sum of the covalent radius (0.3 Å) or the van der Waals radius (1.2 Å) of the hydrogen atom and one-half of the van der Waals thickness of the benzene molecule (1.85 Å). The obtained values of the energy of the Coulomb interaction of the hydroxyl group with the benzene molecule for different positions are shown graphically in Fig. 1c.

As is seen from Fig. 1c, the energy of the Coulomb interaction of the hydroxyl group with the benzene molecule, when the hydroxyl group is displaced within the benzene ring, depends little on their mutual position and amounts to about 4-6 kcal/mol. Outside the benzene ring the energy of this interaction decreases rapidly.

An approximate estimate of the energy of other types of interaction of the hydroxyl group with the benzene molecule—polarization and dispersion—showed that the energy of both interactions is about 2 kcal/mol. The repulsion energy is probably of the same order.

Thus, the results obtained show that the energy of the Coulomb interaction of a polar hydroxyl group with a nonpolar benzene molecule, if the actual charge distribution in the benzene molecule is taken into account, is large and, in the formation of a hydrogen bond in this system, apparently plays a determining role among the other interactions (polarization—acceptor-donor, dispersion, and repulsion), which, moreover, must partly compensate one another.

A benzene molecule adsorbed on the surface of a completely hydrated silica gel interacts mainly with one or a few hydroxyl groups, since the area per hydroxyl group on the completely hydrated surface of silica gel is approximately equal to 13 Å^2 ([20]), which is close to that part of the area of the benzene molecule within which the energy of the Coulomb interaction with the hydroxyl group falls to one-half of the maximum value of the energy of this interaction.

An adsorbed benzene molecule on the surface of hydrated silica gel, in addition to interacting with a surface hydroxyl group, also interacts with the remaining atoms forming the particles of the silica-gel framework (chiefly dispersion interaction and

repulsion). Therefore, removal of hydroxyl groups from the surface of silica gel, on the one hand, should lead to a decrease in the heat of adsorption of benzene molecules on the dehydrated surface of silica gel as compared with the heat of adsorption on the hydrated surface, owing to the removal of the interaction of the benzene molecule with the hydroxyl group; but, on the other hand, it should lead to an increase in the energy of interaction of the adsorbed benzene molecule with the bulk phase of the silica gel, since removal of the hydroxyl group from the surface should lead to a certain approach of the benzene molecule to the surface of the silica-gel skeleton particles. Therefore, the experimentally measured difference in the heats of adsorption of benzene vapor on hydrated and dehydrated silica-gel samples will be smaller than the energy of interaction of the benzene molecule with the hydroxyl group of silica gel. In addition, the hydroxyl groups on the surface of silica gel are oriented with respect to the plane of the ring of the adsorbed benzene molecule at different angles, which should lead to some decrease in the energy of this interaction as compared with the energy for the perpendicular direction. An approximate calculation showed that when the hydroxyl group is situated, for example, at an angle of 45° to the plane of the benzene ring, the energy of the Coulomb interaction decreases by approximately 30%.

Taking into account what has been said, as well as the crudeness of the adopted models of the distribution of electric charge both in the benzene molecule and in the hydroxyl group, and the uncertainty of the equilibrium distance $z_{\mathrm{H...C}}$, one may conclude that the calculated energy of the Coulomb interaction (about 4–6 kcal/mole) is in satisfactory agreement with the experimental values of the decrease in the heat of adsorption of benzene upon dehydration of the silica-gel surface (2–3 kcal/mole).

Moscow State University
named after M. V. Lomonosov

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
18 I 1958

CITED LITERATURE

1 A. V. Kiselev, K. G. Krasil' nikov, L. N. Soboleva, DAN, **94**, 85 (1954).
2 A. A. Isirikyan, A. V. Kiselev, DAN, **115**, 343 (1957).
3 L. D. Belyakova, A. V. Kiselev, DAN, **119**, 298 (1958).
4 A. V. Kiselev, *The Structure of Certain Corpuscular Adsorbents and its Influence on their Adsorptive Properties*, Colston Papers, **10**, Bristol, 1958.
5 A. V. Kiselev, DAN, **106**, 1046 (1956).
6 M.-L. Josien, C. R., **237**, 175 (1953).
7 W. Lüttke, R. Mecke, Zs. Elektrochem., **53**, 241 (1949).
8 M. Tamres, J. Am. Chem. Soc., **74**, 3375 (1951).
9 A. N. Terenin, in the collection *Surface Chemical Compounds and Their Role in Adsorption Phenomena*, Moscow, 1957, p. 206.
10 R. S. McDonald, J. Am. Chem. Soc., **79**, 850 (1957).
11 M. Davies, J. Chem. Phys., **15**, 739 (1947).
12 M. M. Jones, W. R. Gilkerson, G. A. Gallup, J. Chem. Phys., **20**, 1048

(1952).
13 J. E. Lennard-Jones, J. A. Pople, Proc. Roy. Soc., A, **205**, 155 (1951).
14 J. A. Pople, Proc. Roy. Soc., A, **205**, 163 (1951).
15 W. S. Fyfe, J. Chem. Phys., **21**, 2 (1953).
16 W. G. Schneider, J. Chem. Phys., **23**, 26 (1955).
17 J. C. Slater, Phys. Rev., **36**, 57 (1930).
18 H. Landolt—R. Börnstein, *Tabellen*, Aufl. 6, 1, Teil 3, S. 506.
19 M. V. Vol' kenshtein, *Structure and Physical Properties of Molecules*, Moscow —Leningrad, 1955.
20 S. P. Zhdanov, A. V. Kiselev, ZhFKh, **31**, 2213 (1957).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.